The Life of an Anise-Flavored Alcoholic Beverage: Does Its Stability Cloud or Confirm Theory?

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The well-known alcoholic beverage Pastis becomes turbid when mixed with water due to the poor solubility of *trans*-anethol, the anise-flavored component of Pastis in the water solution formed. This destabilization appears as the formation of micrometer-sized droplets that only very slowly grow in size, thus expanding the life of the anise-flavored beverage. The slow growth has been attributed to an extremely low interfacial tension of the droplets. Fitting experimental droplet growth rates to an Ostwald ripening model, interfacial tensions were deduced in the past. Direct determination of the interfacial tensions was not yet reported on these systems. We have measured the interfacial tensions and used these data to predict droplet growth rates using an Ostwald ripening model and a model for creaming of the droplets. The interfacial tension was measured to be about 11 mN/m for a 30/70 w/w % ethanol/water mixture, and it decreases slightly to a value of 1.4 mN/m in the case of a 70/30 w/w % ethanol/water mixture. These values are not as low as those deduced in the past. The theoretical predictions for both the Ostwald ripening rates and the creaming rates, using the directly measured interfacial tensions, are found to contradict with the experimental results on Ostwald ripening and creaming. While the experiments on Ostwald ripening show an increase in stability with increasing ethanol concentration, the results based on our interfacial tension measurements in combination with the same Ostwald ripening model show a decrease in stability with an increase in ethanol concentration. Further research is needed to understand fully which parameters play a role in both droplet growth and the stability of these three-component emulsions to elucidate the current discrepancy between model and experiment. This could be useful for a better control of "spontaneous emulsification" processes.

1. Introduction

In Mediterranean countries, anise-flavored alcoholic beverages are frequently consumed. These beverages include, for example, Pastis, Pernod, Ricard (in France), Ouzo (in Greece), Raki (in Turkey), and Sambuca (in Italy). All appear transparent when bottled, with an ethanol content around 40% (v/v). Many manufacturers offer advice to drink this Pastis-like beverage (PLB) with the addition of water (dilution of about 5 times), after which the drink spontaneously changes into an opaque, milky white solution. This phenomenon is known as the Pastis effect[1] or Ouzo effect.[2,3] Some research has been performed on this beverage to gain insight into this physical phenomenon. When bottled, PLBs are three-component homogeneous solutions composed of water (about 55%), alcohol (about 45%), and "oil" (about 0.1%). This "oil" consists mainly of *trans*-anethol, which is an ester with a very specific odor that gives its unique anise smell to these beverages. Anethol is soluble in ethanol but extremely insoluble in water (calculated log *P* of 2.91). When bottled, the ratio between the ethanol, water, and oil is chosen in such a way that the oil is still soluble in the mixture, so the mixture appears transparent. However, when the alcoholic beverage is poured into water, the oil is no longer soluble. This

causes the oil droplets to form in the solution due to the supersaturation of the oil. The tremendous decrease in solubility due to the addition of water causes a very large supersaturation, so that many nuclei form from small fluctuations in concentration. Although the amount of oil is small, it results in the appearance of a large number of small droplets, since the initial rate of nucleation is extremely large. These droplets are of the order of the size of 1 μm or less. Due to the many droplets in the solution, visible light gets multiply scattered within the solution, and the resulting diffusive motion of the light makes the solution to appear milky white. The systems created by addition of water to PLBs can therefore be regarded as emulsions, where the oil is distributed as small droplets in another liquid. However, there is a distinct difference between most food emulsions and the emulsions created by the addition of water to PLBs. The first difference is that most food emulsions are stabilized (indeed it is only metastability) by one or more surfactants that migrate toward the water/oil interface, whereas the emulsion formed from PLBs does not contain an emulsifier. The second difference is that, to make normal emulsions with droplet sizes of the order of 1 μm, energy (e.g., mechanical energy such as in homogenization) is required to compensate for the important increase in surface energy (about 1 J for a 100 mL drink). However, the emulsification process of the PLB mixing with water does not require the addition of any form of mechanical energy. Therefore, this process is called "spontaneous emulsification". It is nowadays frequently used for the production of nanocapsules and nanoparticles,[4,5] which makes it possible to create particles smaller than those created with conventional methods, such as solvent

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evaporation techniques. This technique can also be used to create small nanospheres, liposomes, and vesicles.[4]

Measurements performed with various techniques, such as small angle light scattering, small angle neutron scattering, electrical resistance, and dynamic light scattering, mostly show that the droplet diameters are of the order of 1 μm,[1,2,3,6] though some experiments even show that the size of the droplets can be as small as 200 nm.[6] This is rather small, as no mechanical agitation is used. Several experiments have followed the increase of the size of the droplets with time. Although the size appears to increase slightly in the beginning, it stabilizes after a few hours; PLB-based emulsions can then stay stable for days, weeks, or even months. The initial size of the droplets and the droplet size obtained after stabilization depend on the ethanol/water ratio and the amount of oil present in the system. Experiments[1,3] also indicated that the growth of the droplets immediately after nucleation of the oil is obtained via a process called Ostwald ripening rather than through droplet coalescence. Both coalescence and Ostwald ripening can be studied by monitoring the droplet size with time. Droplet growth via coalescence occurs due to the merging of two or multiple droplets, and the volume of the droplets increases exponentially in time. The growth of the droplets due to Ostwald ripening does not depend on the merging of droplets but rather by the diffusive transport of the dissolved oil through the medium, and this process is characterized by a linear droplet growth in time.

Sitnikova et al.[3] showed that the growth rate of droplet size was characterized by a linear growth with time, and they determined the Ostwald ripening rate. From this rate, they deduced an estimation for the interfacial tension in PLB emulsions, which they found to be less than 1 mN/m. They ascribed the stability of these emulsions to this low interfacial tension. However, the interfacial tension in these systems was not determined yet. In this paper, we address the determination of the interfacial tension of these three-component systems and we give the results of interfacial tension measurements between *trans*-anethol and different ethanol/water mixtures. Using these experimental values for the interfacial tension, we make theoretical predictions for droplet growth and compare these with experimental results.

2. Experimental Section

2.1. Materials. *trans*-Anethol was purchased from Sigma. Ethanol (98.8%, technical grade) and demi-water were used. Stabilization experiments were performed using commercial Pernod.

2.2. Interfacial Tension. An automatic drop tensiometer (ADT) was used to measure the interfacial tension between the oil and the ethanol/water mixtures. This system can follow the interfacial tension and the volume of the droplet in time. Measuring such quantities for three-component systems is not straightforward. Because of the high solubility of *trans*-anethol in ethanol and its poor solubility in water, the total solubility of the oil in any ethanol/water mixture is determined by the composition of the mixture. It is therefore not possible to measure the interfacial tension directly between the oil phase and any ethanol/water mixture, since the oil will partially dissolve in the mixture. Measuring the interfacial tension between two phases requires equilibrium between two liquids, which in the case of oil and ethanol/water mixtures is clearly impossible. To avoid diffusion of the oil into the ethanol/water mixtures due to partial solubility, we first saturated our ethanol/water mixtures with *trans*-anethol to suppress the diffusion of the oil into the ethanol/water mixtures during the measurements. In addition, this presaturation mimics the end situation of having poured Pernod into water, since it may be assumed that in that case, after nucleation of oil droplets has taken place, the remaining still solubilized oil within

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the continuous phase is also at its saturation level. To saturate the ethanol/water mixtures, we added an excess of *trans*-anethol to the solution. The mixtures were then heated up to 35 °C, 10 °C above the desired temperature of the experiments, to increase the solubility of the oil into the mixtures. This ensured full saturation of the mixtures when the temperature was lowered down to 25 °C. The excess *trans*-anethol was centrifuged down, as the density of the used ethanol/water mixtures was lower than that of the oil. The oil-saturated mixtures were then poured into a cuvette. A millimeter-sized droplet of *trans*-anethol was inserted in the ethanol/water mixtures using a syringe, equipped with a needle, and its size was determined by the software. Since ethanol is soluble in the oil droplets, little diffusion of ethanol into the droplets was expected. We therefore measured the volume of the droplet and the interfacial tension in time. As the volume of the droplets (and the interfacial tension) did not change significantly during time, we assumed the system to be in equilibrium. Since the size of the droplet did not change, we assumed the density of the oil droplet to be unchanged and constant throughout the time span of the experiment. The droplet size and its shape were then used to calculate the interfacial tension with the use of the density difference between the *trans*-anethol and the ethanol/water mixtures.

In practice, the ethanol/water mixtures were poured into a sample holder of a few milliliters. A syringe with a curved needle was inserted into the mixture. The end of the needle was facing up so that the droplets were placed on top of the needle. Using a needle facing upward prevents the droplets from falling down, and gives the droplet a more oblate spheroid shape rather than a prolate spheroid shape, since gravity is pulling the droplets down. Although this technique can be used to measure the interfacial tension of these mixtures, the experimental setup has its limitations. Increasing the amount of water in the ethanol/water mixtures decreases the density difference between the oil and the mixtures (a mixture of about 90% would have the same density). Since the shape of the droplets is determined among others by the density difference of the two phases, decreasing the density difference between the two phases will induce the shape of the droplet to become more spherical. Since the software of the ADT needs a certain minimal deformation to determine the interfacial tension, the output of the software becomes unrealistic when the density difference becomes too small. On the other hand, when the density difference is too large, the droplets are pulled down by gravity and the droplets fall of the needle before they reach a size large enough to be measured. These limitations narrow the range of compositions to be measured with this experimental setup.

2.3. Density. To calculate the interfacial tension between the two phases, the density difference between the two phases is needed. The density of the anethol was determined with the use of an Anton Paar density meter 5000 to be equal to 0.9881 g/mL. The densities of the used ethanol/water mixtures were also determined with the density meter. All densities were measured at room temperature (25 °C).

2.4. Stability Experiments. We performed stability experiments with commercially available Pernod. We used three different dilutions of the PLB in water to investigate the effects of the added amount of water on the stability of the emulsion: 1:1, 1:2, and 1:3 (v/v). The ethanol/water ratios were 20/80, 16/84, and 10/90 (v/v). The total volume was kept constant. The stability of the emulsions was checked by eye.

3. Results and Discussion

3.1. Interfacial Tension Measurements. We measured the interfacial tension between *trans*-anethol and nine ethanol/water mixtures with different compositions. The different ethanol/water mixtures were saturated with *trans*-anethol, and the density of the mixtures was determined. The density of *trans*-anethol was determined to be 0.9881 g/mL, from which the density differences with the ethanol/water solutions were determined (Table 1).

As can be seen in Table 1, the interfacial tension is approximately equal to 11 mN/m when the ethanol/water composition has a ratio of 30/70 w/w %. For 20/80, no

Table 1. Ethanol/Water Ratio, Density of the Ethanol/Water Mixture, Density Difference with the Density of the Oil, and Interfacial Tension between the Oil Phase and the Ethanol/Water Mixture[a]

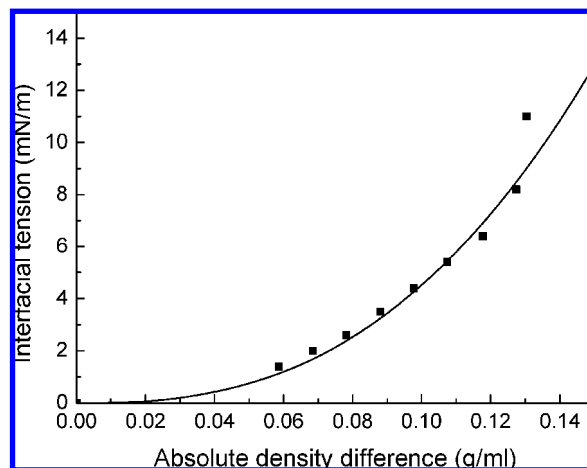| sample no.	ethanol/water ratio (w/w %)	density (g/mL)	density difference (g/mL)	interfacial tension (mN/m)
1	20/80	0.9667	0.0214	(20)
2	30/70	0.9540	0.0341	11
3	35/65	0.9450	0.0431	8.2
4	40/60	0.9353	0.0528	6.4
5	45/55	0.9250	0.0631	5.4
6	50/50	0.9154	0.0727	4.4
7	55/45	0.9056	0.0825	3.5
8	60/40	0.8958	0.0923	2.6
9	70/30	0.8762	0.1119	1.4
10	80/20	0.8567	0.1314	
11	100/0	0.8176	0.1705	

[a] Confidence intervals on interfacial tension are about 10%.

reproducible value for the interfacial tension was obtained, probably because the difference in density is too small. Adding more ethanol decreases the interfacial tension to a value of 1.4 mN/m. The addition of water increases the interfacial tension, which seems to appear in a nonlinear fashion. This could indicate that the system shows critical behavior in a similar way as, for example, water-in-water emulsions do.[7,8] These emulsions show very low interfacial tensions with values below 1 μN/m. If the system indeed shows critical behavior, then it should obey the following relation

$$\gamma \sim \Delta\rho^{\mu/\beta} \tag{1}$$

in which μ/β is the critical exponent, which was determined to be 3 from mean-field theory and 3.9 from the Ising model.[9] From this equation, we see that when the density difference approaches 0, the interfacial tension should vanish. However, in the Pastis problem, the interfacial tension should vanish in a pure ethanol solution, since the oil is completely soluble in ethanol. However, in this case, the density difference between the oil and the ethanol is not 0. Therefore, we used the density of an ethanol/oil mixture as the reference mixture where the interfacial tension should be 0 (rather than the density of pure ethanol). We calculated the density of the reference mixture by extrapolating the densities of the ethanol/water/oil mixtures. This value is given in Table 1 as sample number 11. The difference between this density and the density of the oil (0.1705 g/mL) was taken as the reference density difference (0). The other densities were normalized by taking the absolute density difference between the density difference of the mixture with the oil, and our reference mixture (ethanol/oil). We plotted the interfacial tension (γ) versus the absolute density difference ($|\Delta\rho|$) in Figure 1, and the experimental data points were fitted to $\gamma \sim |\Delta\rho|^{\alpha}$, where α was found to be 2.5, in reasonable agreement with the value of 3 found from mean-field theory. This is one first indication that the three-component oil/water/ethanol mixture can be considered to be near-critical. As far as the authors know, phase-separated water-in-water emulsions showed this near-critical behavior,[7,8] but it was not reported previously for oil/water emulsions.

3.2. Droplet Growth Due to Ostwald Ripening. When a PLB is poured into water, the reduced solubility of the oil in the

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Figure 1. Interfacial tension, γ, plotted versus the absolute density difference $|\Delta\rho|$. The squares refer to the experimental data points. The line is the best fit to $\gamma \sim |\Delta\rho|^{\alpha}$.

solution formed results in the supersaturation of the oil and in the appearance of numerous small droplets. Sitnikova et al.[3] measured the droplet sizes in these anethol/water/ethanol mixtures and found them to be less than 1 μm. They observed that the droplets grow in time, and they measured the initial growth rate of these droplets using photon correlation spectroscopy. Depending on the composition of the mixture, the initial average radius was approximately 500 nm and droplet growth was followed until the final size was between 1 and 1.5 μm (after a few days). On larger time scales (5–30 days), the apparent droplet size did not increase any further. Droplet growth was found to be governed by the Ostwald ripening process, as the growth rate showed a linear dependence in time.[3] This Ostwald ripening process is governed by the diffusion of the dissolved oil through the dispersion medium. Ostwald ripening occurs as a consequence of the difference of the chemical potential within the droplets, which depends on the curvature of the droplets (Kelvin effect). Concentration gradient results in the diffusion of the dispersed material from the smaller droplets through the medium into the larger droplets, which leads to the growth of the bigger droplets at the expense of the smaller ones. The kinetics of this diffusion process is most often described in terms of the Lifshitz–Slyozov–Wagner theory (LSW), which states that the volume of droplets with radius R increases linearly with time as

$$R^3 = R_0{}^3 + K_{\mathrm{ow}}t \tag{2}$$

in which R_0 is the initial droplet size and K_{ow} is a specific constant. In coarsening due to Ostwald ripening, the specific constant is known as the Ostwald ripening rate, ν, which can be given by

$$\nu = \frac{8\gamma V_{\mathrm{m}} D C_{\infty}}{9RT} \tag{3}$$

in which γ is the interfacial tension, V_{m} is the molar volume of the dispersed phase, D is the diffusion coefficient of the dispersed-phase molecules in the continuous phase, C_{∞} is the solubility of the dispersed phase in the continuous medium, R is the gas constant, and T is the temperature. The LSW theory is based on the following assumptions: (i) molecular diffusion is the rate-determining phenomenon for the transport of material between the particles; (ii) there are no particle interactions, that is, the system is infinitely dilute; (iii) the particles are spherical and fixed in space; and (iv) the concentration of solubilized material
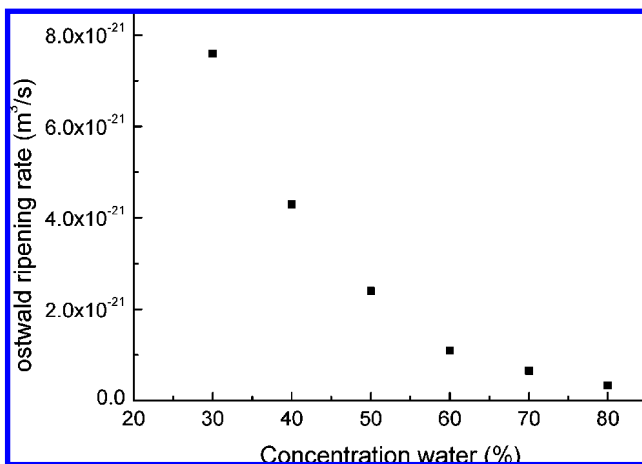
Figure 2. Ostwald ripening rate, ν, versus the concentration of water of the ethanol/water mixtures.

Table 2. Ethanol/Water Ratio, Solubility of *trans*-Anethol in the Ethanol/Water Mixture, Interfacial Tension, and Growth Rate of the Ostwald Ripening Process

sample no.	ethanol/water ratio (w/w %)	solubility C_∞	interfacial tension γ (N/m)	growth rate ν (m³/s)
1	20/80	0.3×10^{-3}	20×10^{-3}	3.3×10^{-22}
2	30/70	1×10^{-3}	11×10^{-3}	6.5×10^{-22}
4	40/60	3×10^{-3}	6.4×10^{-3}	1.1×10^{-21}
6	50/50	1×10^{-2}	4.4×10^{-3}	2.4×10^{-21}
8	60/40	3×10^{-2}	2.6×10^{-3}	4.3×10^{-21}
9	70/30	1×10^{-1}	1.4×10^{-3}	7.6×10^{-21}

is a constant throughout the dispersion medium, except for the direct surroundings of the particles.

We assume that V_m and D are constants that are independent of the composition of the continuous medium (ethanol/water), so besides the determined interfacial tension the solubility of the dispersed oil droplets in the medium gives all required information to calculate the Ostwald ripening rates for different compositions. Using the partial phase diagram of Sitnikova et al.,[3] we have determined this solubility of the oil in different ethanol/water mixtures (Table 2).

In Table 2, we see that the solubility decreases substantially with increasing water concentration. However, Figure 1 shows that increasing water concentration increases the interfacial tension. According to eq 3, this increase in interfacial tension should increase the Ostwald ripening rate instead of decreasing it. Thus, interfacial tension and oil solubility have a counteracting effect on the Oswald ripening rate, and the interplay between the two parameters determines the total Ostwald ripening rate. Using a value of 1×10^{-9} m²/s for the molecular diffusion coefficient (based on a molecular radius of 0.25 nm), a value of 1.5×10^{-4} m³/mol for the molar volume V_m, and 298 K for the temperature T, we calculated the Ostwald ripening rate for the different compositions of the ethanol/water mixtures (Figure 2).

From the results in Figure 2, we can see that the Ostwald ripening rate decreases with increasing concentration of water, which indicates that the solubility of the oil in the medium plays a more important role than the interfacial tension in the case of these three-component systems. However, when we look at the experimental results reported by Sitnikova et al.,[3] we see that the rate actually increases with increasing concentration (keeping the weight fraction of oil constant). Thus, the experiments are not in agreement with the theoretical predictions of eq 3. One might argue that eq 3 ignores the interaction between droplets and has to be extended with a factor compensating for these

droplet interactions. Taylor,[10] Baldan,[11] and Voorhees[12] give a recent overview of this shortcoming of the LSW theory. In neither of these theories that take into account droplet interaction, this factor compensating for the volume would have a value higher than two. For the volume fractions used in our model systems, the value for this factor is that low that the volume fraction factor can be discarded from the theory (as was also mentioned by Sitnikova et al.[3]). Even if the interactions between the droplets do play a role, the effect would be the same for systems using a fixed oil concentration and can therefore not be responsible for the discrepancy between the experimental and theoretical results.

Another process that is discussed in theory that might influence the Ostwald ripening behavior is the emulsifying effect that can occur in systems with multiple components. The LSW theory was developed for single-component droplets. However, the emulsions created by the PLB are three-component systems. Since ethanol is miscible with water as well as with anethol, it might act as an emulsifier, which influences the dynamics of such systems. As the droplets become smaller, the concentration of ethanol at the interface of the oil droplets might increase due to the decrease of the surface of the droplets. Due to the change in concentration of ethanol at the droplet surface, the interfacial tension of the mixtures might change as the sizes of the droplets change in time, leading to a time-dependent interfacial tension $\gamma(t)$. However, if this phenomenon would occur in our systems, the time-dependent interfacial tension would affect the scaling of the growth rate, as was discussed by Yao and Laradji[13] and shown by de Smet et al.[14] Since the results from Sitnikova[3] do not show a deviation from the linear dependence of the growth rate, we can conclude that this effect does not occur in our systems, and we cannot explain the deviations in the experimental and theoretical results.

Due to the miscibility of anethol and ethanol, it might be possible that ethanol is more concentrated in the oil droplets than in the ethanol/water solution. In this case, the ethanol/water ratio would change and there would be an overestimation of the solubility. However, since the volume fraction of the oil is less than 1%, it is hard to believe that a possible disproportionation of ethanol would be able to make a large difference in the solubility, and we therefore do not think that this could influence the Ostwald ripening to a significant extent.

3.3. Droplet Growth Due to Creaming. The Ostwald ripening rate as discussed so far describes the growth of droplets at short time scales in the beginning of the process, and the stability of the emulsions depends on the growth of the droplets. At longer time scales, the stability of the emulsions is influenced by droplets creaming, for which the rate can be given by Stokes' law:

$$U = \frac{2gR^2(\rho_2 - \rho_1)}{9\eta_1} \tag{4}$$

where U is the mean droplet velocity, g is the gravitational constant, R is the radius of the droplet, ρ_2 is the density of the dispersed phase, and ρ_1 and η_1 are the density and the viscosity of the continuous medium, respectively. Assuming the droplet size to be 1 μm, taking a viscosity of 1 mPa·s and taking the densities of the phases from Table 1, we have estimated the stability of the different mixtures (Figure 3).
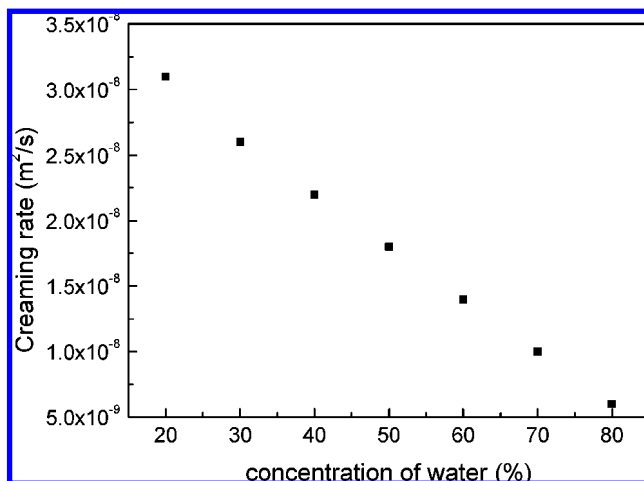
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Figure 3. Droplet velocity, *U*, versus the concentration of water in the ethanol/water mixtures.

To see whether these theoretical predictions based on the later stage of the droplet growth agree with experiments, we performed some simple stability experiments. For these experiments, we used the commercial Pernod instead of the model system with *trans*-anethol. We mixed Pernod with water in the ratios 1:1, 1:2, and 1:3 (with a fixed total volume; the ethanol/water ratios were 20/80, 16/84, and 10/90 (v/v), respectively). Since the concentration of the oil in the commercial product is only about 0.1%, we expected the size of the formed droplets after the initial Ostwald ripening process to be the same and we assumed that volume fraction effects were negligible. The stability of the emulsions was determined by examination of the turbid emulsions by eye. The emulsions were considered to be phase-separated when the mixtures became transparent. Although this transparency alone does not totally confirm that the solution is phase-separated, it still is a good indication. Since the concentration is not changed and the number of droplets does not seem to decrease in time, the decrease in turbidity most likely is caused by creaming of the droplets in time. The mixture with the highest amount of water (1:3) was found to be transparent after little more than one week, while the system with the least amount of water (1:1) became transparent only after more than 3 weeks. Thus, experimentally, the system with the least amount of water was found to be most stable. However, care must be taken in drawing conclusions from these experiments. Since commercial Pernod has other food additives besides *trans*-anethol, the stability of the emulsion might be different from those of pure three-component systems. These impurities might have an influence on crystallization or stabilization of the emulsion and could also alter the densities within the system. However, since the impurities should be similar for all three compositions, the effect is expected to be the same. Therefore, we believe that the trend of the stability versus the density difference (or water concentration) in the real commercial system can be compared to the trend of the pure system. Another point of concern that might be imported into the interpretation of the results is the viscosity of the mixture. Ethanol/water mixtures are known to have an anomalous mixing behavior. Tanaka and co-workers[15] have shown that the viscosity of ethanol/water mixtures at 25 °C changes from 0.9×10^{-3} Pa·s for pure ethanol to 1.1×10^{-3} Pa·s through a maximum of 2.3×10^{-3} Pa·s for a 20/80 ethanol mixture (mole fraction). However, in the region of our experiments between 20/80 (v/v) and 10/90 (v/v) (which corresponds to a mole fractions of 0.035 and 0.07,

respectively), the viscosity changes from 1.4×10^{-3} to 1.15×10^{-3} Pa·s. The difference between these two values is only approximately 20%, which does not seem to be able to explain the discrepancies between experiment and theory. However, the viscosity of the mixture might have an influence on the stability behavior.

From the calculations using eq 4, we see that the creaming rate should decrease with increasing water concentration, due to the decrease in the density difference between the ethanol/water mixtures and the *trans*-anethol. Even though issues such as impurities and viscosity effects have to be taken into account, the systems do not seem to become more stable when the water concentration increases. So, it seems that stability as determined in experiments with the commercial systems is not in agreement with predictions of stability due to creaming of the pure systems. Thus, for these three-component emulsions, the theoretical predictions on both the droplet growth due to Ostwald ripening and the stability of the emulsions due to creaming do not seem to be consistent with experimental results.

3.4. Experiment versus Theory. The stability of these three-component emulsions due to droplet growth and creaming determined by theoretical predictions does not seem to conform to experimental results. Even taking into account possible effects of droplet interactions due to volume fractions and the change of interfacial tension due to emulsifying properties is not sufficient. Although a lot of research has been done theoretically and experimentally to gain more insight into the Ostwald ripening process, a full understanding of the parameters that are involved is still lacking. Sitnikova et al.[3] already showed that, in three-component mixtures such as ours, the weight fraction of the oil has a much greater effect on the Ostwald ripening rate than predicted with most theories. Their results also showed that, at fixed oil volume fraction and varying ratio of the ethanol/water mixtures, droplet growth decreases with increasing ethanol concentration. They stated that this is in accordance with the LSW theory, since the interfacial tension decreases as the concentration of ethanol increases. However, although this is true, they have not taken into account the fact that the solubility of the oil increases significantly with increasing ethanol concentration. Taking this into account, we showed that theoretical calculations show exactly the opposite situation: the droplet growth increases with increasing ethanol concentration. So, obviously, for these three-component systems, the Ostwald ripening process cannot simply be described by available theories. In our calculations, we have assumed that the diffusion of the oil is constant and is independent of the composition of the medium. However, Yu and Yurtov[16] performed Ostwald ripening experiments in water-in-oil emulsions, and their results showed that the diffusion coefficients of the dispersed phase can be up to 1000 times smaller than the calculated molecular diffusion coefficient. If the diffusion coefficient would not be constant and would be dependent on the compositions of the continuous medium, this would have major consequences for the calculations of the Ostwald ripening rates. Especially, comparing rates between systems having different compositions would lead to different conclusions. However, research on the effect of the diffusion coefficient has not been performed extensively, and the effect on the Ostwald ripening rate is not known. One route of explanation of the discrepancy between experiment and theory might lie in the fact that one has to consider the system not being solely an emulsion but that one has to take into account the fact

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(16) Yu, M.; Yurtov, E. *Colloid J.* **2003**, *1*, 35−39.

that part of the oil is present in the form of nanodroplets,[18] which do not exhibit creaming. Carteau and co-workers[18] recently used NMR spectroscopy to investigate the phase separation process and observed that in the very early stage (the first 30 min) the majority of the oil is present in the form of small aggregates. These small aggregates nucleate to form bigger droplets, after which Ostwald ripening starts. The presence of these small aggregates might have an influence on both the Ostwald ripening and the creaming behavior of the emulsions.

As was already mentioned, these three-component emulsions are of great interest, since they have unique properties. These emulsions, formed by spontaneous emulsification, are stable for a very long time (they have been known to be stable for more than months[3]) without being thermodynamically stable. The droplets have sizes of less than 1 μm, which is remarkable since no mechanical agitation is applied to create such small droplets (no homogenization or stirring). As was shown in this article, the stability of these emulsions is determined by two phenomena: the Ostwald ripening in the beginning of the process and the creaming of the droplets in the late stage.

Although a lot of research has been done on the Ostwald ripening rate (good reviews were published by Taylor,[10] Baldan,[11] and Voorhees[12]), both theoretically and experimentally, the results described in this article show that there is still discrepancy between theoretical calculations and experimental results, which was also observed by others.[10,12,17] The authors believe that the theories available in the literature are not sufficient to explain the results for these unique three-component systems, and understanding of the properties of these systems is desirable, since the spontaneous emulsification process can be used for many practical situations, such as for the design of drug-loaded particles, pharmaceutical-filled capsules, and vesicles or for the production of size-controlled polymer particles. This process could be used in a variety of fields, such as the food and polymer industry but also in cosmetics and agricultural applications. More knowledge of the parameters that determine the stability of these emulsions, besides interfacial tension, solubility, and density difference, might lead to better control of the emulsification process.

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(18) Carteau, D.; Pianet, I.; Brunerie, P.; Guilemat, B.; Bassani, D. M. *Langmuir* **2007**, *23*, 3561−3565.

4. Conclusion

In this article, we measured the interfacial tension of a three-component system containing the oil *trans*-anethol, water, and ethanol. We measured the interfacial tension between the oil phase and different ethanol/water systems. It was found that the interfacial tension decreases with increasing ethanol concentration. Using the solubility of the oil in the different ethanol/water systems, we calculated the Ostwald ripening rate of these emulsions. The results show that the growth rate of the droplets due to Ostwald ripening decreases as the concentration of water is increased, which can mainly be ascribed to the large decrease in the solubility of the oil in the medium as the concentration of the water is increased. However, experiments show exactly the opposite results; the growth rate of the droplets decreases with increasing ethanol concentration. Using the density difference between the oil phase and the ethanol/water phase, we also calculated the creaming rate of droplets. The theoretical calculations show that the creaming rate decreases with increasing concentration of water. These results lead to the same conclusion as the calculations of the Ostwald ripening rate; increasing the ratio of water leads to more stable emulsions. However, also in this case, experiments show the opposite result; increasing the amount of ethanol leads to an increase in the stability of the emulsions. Therefore, currently available theories do not seem to explain the results for these unique three-component systems. Besides the interfacial tension, the solubility of the oil in the medium, and the density difference between the oil and the medium, other parameters might play a role in these multiple-component systems. These parameters might influence both the Ostwald ripening process and the creaming of emulsion droplets.

Note Added in Proof. We thank Prof. E. Dickinson for pointing out the following. According to the article by Block et al., different gradients of concentration, density, and pressure are present in critical systems. As our system shows critical behavior indicated by interfacial tension measurements, these gradients can influence the system in such a way that normal Ostwald ripening theory might not be applicable to our systems. (Block, T. E.; Dickinson, E.; Knobler, C. M.; Schumaker, V. N.; Scott, R. L. *J. Chem. Phys.* **1977**, *66*, 3786.)